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| <b>(51) International Patent Classification 5 :</b><br><b>B41M 5/00</b>  | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 92/07723</b><br><b>(43) International Publication Date:</b> 14 May 1992 (14.05.92)  |
| <b>(21) International Application Number:</b> PCT/US91/08168<br><b>(22) International Filing Date:</b> 1 November 1991 (01.11.91)<br><br><b>(30) Priority data:</b><br>608,049 1 November 1990 (01.11.90) US<br>776,148 15 October 1991 (15.10.91) US<br><br><b>(71) Applicant:</b> VAN LEER METALLIZED PRODUCTS (USA) LIMITED [GB/US]; P.O. Box 9321, Framingham, MA 01701-0321 (US).<br><br><b>(72) Inventor:</b> FITCH, John, J. ; 177 Hartford Street, Natick, MA 01760 (US).<br><br><b>(74) Agents:</b> PATCH, Robert, J. et al.; Young & Thompson, Suite 200, 745 South 23rd Street, Arlington, VA 22202 (US). |           | <b>(81) Designated States:</b> AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL (European patent), NO, PL, RO, SD, SE (European patent), SN (OAPI patent), SU <sup>+</sup> , TD (OAPI patent), TG (OAPI patent).<br><br><b>Published</b><br><i>With international search report.<br/>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| <b>(54) Title:</b> METHOD OF FORMING A COATED SHEET WHICH WICKS AWAY OIL AND PRODUCT THEREOF   |           |   |
| <b>(57) Abstract</b><br><br>A coated sheet for decorative or informational applications is formed of an oil absorbing substrate and an oil permeable decorative layer. The decorative layer is a porous oleophilic membrane formed from fused polymer particles. Skin oil and certain other liquids placed on the exposed surface of the decorative layer are absorbed into the sheet so that they do not appear on that surface and do not interfere with the optical effect of diffraction gratings or holograms thereon.  |           |   |

METHOD OF FORMING A COATED SHEET WHICH WICKS AWAY OIL AND  
PRODUCT THEREOF  
SPECIFICATION

1 Field of Invention:

This invention relates to the decoration of sheeting, and more particularly to the decoration of materials such as standard, light weight, cellulosic sheets (paper). This invention also relates to the embossment of sheets or films, and more particularly to the wicking away of oil from the decorative surface of sheets or films.

Description of the Prior Art:

Cellulosic sheets are normally decorated by imprinting. To achieve certain special effects, the imprinting requires special inks and relatively complex printing procedures. In addition, some decorative effects can not be realized by imprinting. One very desirable decorative effect is the iridescent visual effect created by a diffraction grating. This striking visual effect, attributed to Sir John Barton, Director of the British Royal Mint (circa 1770), occurs when ambient light is diffracted into its color components by reflection from a diffraction grating. A diffraction grating is formed when closely and regularly spaced grooves (5,000 to 11,000 grooves per cm.) are embossed on a reflective surface.

In recent times, this diffraction grating technology has been employed in the formation of two-dimensional holographic images which create the illusion of a three-dimensional image to an observer. This holographic image technology can form very attractive displays. Furthermore, because the economics of forming holographic images is significantly dependent upon economies of scale, the concept of using holographic images to discourage counterfeiting has found wide application.

expensive and introduces a number of practical problems into the manufacture of embossed sheets.

These and other difficulties experienced with the prior art chemical processes have been obviated in a novel manner by the present invention.

5 It is accordingly an object of the present invention to provide a decorative surface system in which oil, which is deposited on the surface, is wicked away from the surface.

It is a further object of the present invention to provide a decorative surface system in which oil, which is deposited on the surface, does not interfere with the optical effect created by embossed diffraction patterns or holographic images which are present  
10 on the surface.

With the foregoing and other objects in view, which will appear as the description proceeds, the invention resides in the combination and arrangement of steps and the details of the composition hereinafter described and claimed, it being understood that changes in the precise embodiment of the invention herein disclosed may be made within  
15 the scope of what is claimed without departing from the spirit of the invention.

#### SUMMARY OF THE INVENTION

In accomplishing the foregoing and related objects, the present invention provides for embossing the coating of a substrate, such as paper sheeting. The coating is a thermosensitive material which has discernable thermoplastic properties. The term  
20 "thermoplastic", as used hereinafter, shall be construed to include such materials.

The paper advantageously is supplied with the coating of thermoplastic material. The thermoplastic coating is typically applied in a water base or other suitable liquid by gravure, or reverse roll methods.

The actual formation of the coating would begin by spreading a pre-membrane  
25 composition, formed of a dispersion of polymer spheres in evaporable liquid, onto the

FIG. 4 is a perspective illustration of an alternative form of embossment;

FIG. 5 is a cross-section of a laminate showing the substrate and the pre-membrane layer;

FIG. 6 is a cross-section of the laminate after the pre-membrane coating has been  
5 fused to form a porous membrane;

FIG. 7 is a cross-sectional view of the laminate after embossing;

FIG. 8 is a cross-sectional view of the laminate after embossing and after a drop of human skin oil has been deposited on the embossed surface;

FIG. 9 is a cross-sectional view of the laminate showing the oil being wicked away  
10 from the embossed surface;

FIG. 10 is a cross-sectional view of the laminate showing the oil having been wicked to and absorbed by the substrate.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

The preferred embodiment of the present invention begins with the coating  
15 process set out in FIG. 1. Standard paper sheeting 10 is provided with a thermoplastic pre-membrane coating 11, for example, by pouring the liquid pre-membrane mixture from a feed box 12 onto the upper surface 13 of the paper sheeting 10. The thermoplastic coating 11 may also be applied in a solvent or water-base using gravure, or reverse roll methods, represented schematically by the feed box 12.

20 Paper sheeting 10 thickness usually varies from about 40 microns to about 100 microns. The paper sheeting 10 can also be cardboard stock having a thickness up to about 750 microns (note: 25.4 microns = 0.001 inch). The coating weight of thermoplastic coating 11 should be sufficient to accept and retain the microembossed image; rougher papers require thicker thermoplastic coatings. On the other hand, higher

carrier) still present in the mixture after the coating operation and the fusing of the thermoplastic particles which are a primary component of the pre-membrane mixture. The resulting coating is a porous membrane firmly attached to the substrate.

After the softened thermoplastic layer has been coalesced to a porous membrane, 5 the resulting laminate would normally be fed directly to the embossing step. However, it would be possible to allow the resulting laminate to be cooled down and stored so that the embossing step might take place at some later time.

It is more energy efficient, and therefore preferred, to feed the softened and fused laminate directly to the embossing step.

10 Referring now to FIG. 3, once the outer layer 11 of thermoplastic has been softened and fused to a porous membrane, an embossing arrangement is employed for decoration. The arrangement uses a heated platen 32, an embossing roll 31, and a pressure nip roll 33. The embossing roller 31 is a conventional embossing master which has the desired embossing pattern on its surface. This pattern is produced on the roller 15 or rollers by engraving, embossing with a hard material, or mounting patterned plastic films or metal foils on to the surface of the roller 31. When the embossing roller 31 contacts the softened plastic surface 11, the embossing pattern is transferred to the coating 11 on the paper. Simultaneously, the contact with the relatively cooler roller cools the coating. This cooling action prevents flow of the coating after it is removed 20 from the embossing roller. The result is a decorated, polymer coated paper.

The temperature of the embossing master (embossing roller 31) must be below the softening temperature of the thermoplastic coating 11. The temperature of the embossing roller 31, however, should not be so low as to harden the coating 11 before the embossing is completed. It has been found that the preferred temperature for 25 embossing roller 31 (embossing master) can vary depending on its thermoconductivity

opposing roller, i.e., nip roller 33, should be firm, but also somewhat resilient. This allows nip roller 33 to apply a nearly uniform distributed pressure to the back of the sheeting being embossed. It has been determined that nip roller 33 can be quite firm, typically with a Shore A durometer hardness (ASTM D-412) reading of about 70-80, or  
5 even somewhat higher, and yet not so hard as to interfere with attainment of a uniformly distributed pressure on the back of the sheeting being embossed. The contact (dwell) time wherein the embossing roller 31 and nip roller 33 contact the sheeting to achieve embossing, is generally in the range of about 8 milliseconds (E.G., 300 ft./min. for a 1/2 inch wide contact area) to about 0.2 millisecond (e.g., 300 ft./min. for a 1/8 inch wide  
10 contact area).

Various decorative visual effects can be achieved by the embossing. If the diffraction pattern is not to be continuous, a matte background can be provided by suitable modification of the embossing roller. Alternatively, the embossing pattern can, in parts, be filled in with coating material, such as ink or clear lacquer, in those areas  
15 where no embossed decoration is desired.

Turning now to a more microscopic view of the process and product of the present invention, FIG. 5 shows an enlarged cross-sectional view of the substrate 10 which is a paper sheet with a coating 11 of pre-membrane mixture, prior to the fusing of the pre-membrane mixture 11. FIG. 5 shows the thermoplastic spheroids 37, 38, 39,  
20 and 40 which make up the primary component of the pre-membrane mixture 11. The spheroids form the coating 11 on the substrate 10 prior to fusing of the coating.

It should be understood that FIG. 5 is figurative in that it shows the interface between the upper surface 13 of the substrate 10 and the lower layer of the uncured coating 11. Typically, the spheres would be piled up more than forty spheres deep on  
25 the substrate so that the coating is about 20 microns thick.

formed are not vastly different, the visual effect of the grooves beneath the oil is effectively extinguished.

FIG. 9 shows an enlarged cross-sectional view of the laminate of the present invention in which the oil has wetted and been attracted to the internal surface of the pore 46 so that the oil is drawn down into the pore and toward the substrate 10.

FIG. 10 shows an enlarged cross-sectional view of the laminate of the present invention in which the oil 50 has been effectively wicked away from the upper surface of the coating 11, along the pore 46 and completely absorbed by the substrate 10. The result is that the oil which previously disturbed the visual effect on the upper surface of the coating has been completely eliminated from the upper surface of the coating. Applicant has observed a typical transmission rate of between about one half minute and three minutes for finger oil to pass from the surface to the oil absorbing substrate.

The key element of the present invention is the microporous coating which is adapted to absorb, into its pores, any oil which is deposited on its decorative or embossed surface. The polymer from which the membrane is formed must form pores which have pore surfaces which are oleophilic, that is, they must attract or be wetted by human skin oil. In the preferred embodiment, the membrane would be formed by the fusion of thermoplastic polymeric particles of uniform size into the membrane skin populated with pores or microcracks capable of absorbing oil. As seen in Example 1, below, a particle diameter of about 0.5 microns is preferred. Applicant has also noted that the microporous coating has the ability to also transmit gasses, but repel water (hydrophobic). This might also have utility (with or without surface embossing) as a selective membrane in packaging produce by allowing respiration while preventing dehydration.

In the preferred embodiment, the pre-membrane mixture consists of uniform 0.5

or 0.2% of the total mix.

4. Pigment dispersions, (e.g., toluidene red (AIT 222 Day Glo Color Comp.)), can be added directly to the polystyrene/plasticizer mix.
5. A dispersing agent, (e.g., DISPERSE AYD W-28 from Daniel Products) should be added to the plasticizer/polystyrene mix to compatibilize the pigment dispersion with the polystyrene mix.
6. A Defoamer, (e.g., Bubble Breaker 748 from Witco Corp.) is incorporated into the mix after the plasticizer addition.

#### Formulation Data:

- 10 The plasticizer should be charged with the emulsifying agent. The binder is then added to the plasticizer under gentle agitation. Half of the defoamer should be added to the mix, followed by the dispersing agent. The pigment dispersion can be slowly added to the mix, followed by the balance of the defoamer.

#### Misc. Data:

- 15 Two other latices were found to have oil-absorbing properties:
  1. An aqueous dispersion of polyvinyl butyral (Butvar BR from Monsanto). This coating formed a very tacky film.
  2. A carboxylated acrylic copolymer latex, (Hycar 26315 from BF Goodrich) had slower oil absorption than Lytron.
- 20 The primer addition in formulation D adds adhesive strength to the coating. Paper bonds are enhanced if dried at a low temperature (110°C as opposed to 130°C). Reduced gloss and embossed definition result, however.



15

**Formulation B Oil Absorbing Embossable Coating**  
 (Red transparent) % by weight

|                           |  |            |        |
|---------------------------|--|------------|--------|
| <u>Binder</u>             |  |            |        |
|                           | Lytron 2502                            | 79.00      |        |
| <u>Plasticizer</u>        |  |            |        |
|                           | Butyl Benzyl Phthalate                 | 3.9        |        |
| <u>Emulsifying agent</u>  |  |            |        |
|                           | Triton X-100                           | 0.2        |        |
| <u>Pigment Dispersion</u> | Toluidine Red                          |            |        |
|                           | AIT 222 Day Glo Color Corp.            | 15.8       |        |
| <u>Dispersing agent</u>   |  |            |        |
|                           | Disperse AYD W-28 from Daniel Products | 0.3        |        |
| <u>Defoamer</u>           |  |            |        |
|                           | Bubble Breaker 748 from Witco Corp.    | <u>0.8</u> | 100.00 |

**Formulation C Oil Absorbing Embossable Coating**  
 (White translucent) % by weight

|                           |                                   |            |        |
|---------------------------|-----------------------------------|------------|--------|
| <u>Binder</u>             |                                   |            |        |
|                           | Lytron 2502                       | 85.0       |        |
| <u>Pigment Dispersion</u> | Titanium Dioxide                  |            |        |
|                           | WFD - 6102 From Sun Chemical Co.  | 14.5       |        |
| <u>Dispersant</u>         |                                   |            |        |
|                           | Disperse Ayd W-28/Daniel Products | .25        |        |
| <u>Defoamer</u>           |                                   |            |        |
|                           | Bubble Breaker 748/Witco Corp.    | <u>.25</u> | 100.00 |

**Formulation D Oil absorbing Embossable Coating**  
 (Green transparent) % by weight

|                           |                              |      |  |
|---------------------------|------------------------------|------|--|
| <u>Binder</u>             |                              |      |  |
|                           | Lytron 2502                  | 80.7 |  |
| <u>Primer</u>             | Styrene/acrylic dispersion   |      |  |
|                           | in water 49 T 70 from Morton | 2.0  |  |
| <u>Pigment dispersion</u> | (Phthalo Green)              |      |  |

comparative examples.

### EXAMPLE 1

The dispersions and latices of Table 1 were used without additives or modifiers to evaluate the properties of the polymers themselves in producing microembossed coated paper. The dispersions were coated on 35 grams per sq. meter Sibille Stenay clay-coated stock (One Newbury St., Peabody, Massachusetts 01960), using a #12 wire-wound rod. The samples were dried in a 130°C oven for twenty seconds, then embossed at 120°C using a diffraction embossed metallized mylar master. The quality of embossing was evaluated in terms of release of the master from the embossed coating.

10 The embossed coated papers were tested for oil wicking by smearing skin oil across the surface and measuring the time for the diffraction pattern to reappear. Adhesion of the coating to the paper was determined using 3M MAGIC tape (Minnesota Mining & Mfg. Co.) applied with finger pressure and pulled up quickly. The embossed surfaces were photographed at X200 magnification to show their void structure.

15 Both the LYTRON and the ROPAQUE styrene/acrylic copolymer dispersions showed wicking ability. Among the LYTRON dispersions, oil wicking efficiency generally increased as particle size increased.

The LYTRON and ROPAQUE samples evidenced cracking. In contrast, the BUTVAR BR, which showed no cracking, provided very slow wicking. Best results were 20 obtained with the LYTRON 2502 dispersion, which provided excellent oil wicking, low blocking without metal transfer, and good adhesion.

In the Embossing and Adhesion columns of Table 1, "G" indicates "good", "F" indicates "fair", and "P" indicates "poor"; "MT" indicates transfer of metal from the

TABLE 1

| Dispersion     | Particle Size (micron) | Oil Wicking (sec) | Embossing | Adhesion |
|----------------|------------------------|-------------------|-----------|----------|
| Lytron 2101    | .10                    | 240               | G/MT      | G        |
| " 2203         | .20                    | 90                | G/MT      | G        |
| " 300          | .30                    | 105               | G         | G        |
| " 308          | .30                    | 95                | F/MT      | G        |
| " 604          | .30                    | 122               | F/MT      | P        |
| " 2502         | .50                    | 30                | G         | G        |
| " 2705         | .70                    | 24                | G MT      | G        |
| Burvar BR      | .25-1.5                | +300              | G         | P        |
| Adcote 61JH61A | -                      | none              | G         | G        |
| 37R345         | -                      | none              | Blocked   | G        |
| Hycar 26315    | -                      | 120               | Blocked   | P        |
| Unocal 3512    | -                      | -                 | Blocked   | P        |
| Ropaque OP-84  | .55                    | 60                | F/MT      | P        |
| OP-91          | 1.0                    | 67                | G         | P        |

**SUBSTITUTE SHEET**

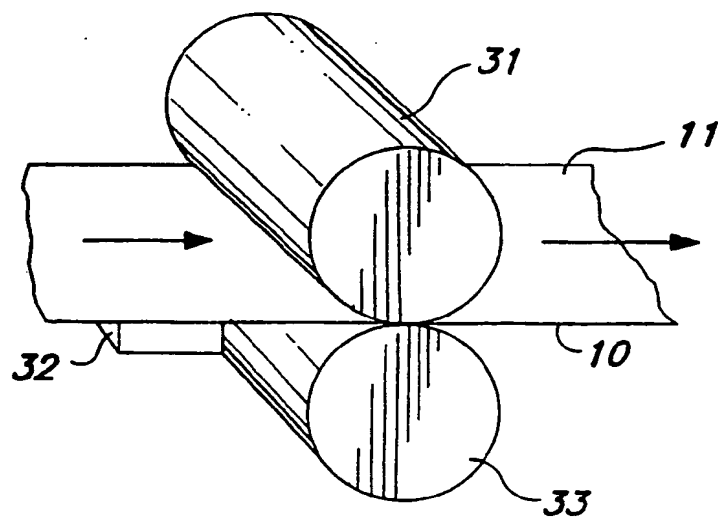
Other aspects of the invention will be apparent to those of ordinary skill in the art. In addition to its manifold decorative applications, the oil absorbing coated sheets of the invention may be employed in applications (e.g., commercial paper) in which security against counterfeiting is desired. This technique may also be used to produce  
5 tamper evident packaging, by using a fragile substrate which would indicate tampering.

The invention, therefore, is not intended to be limited to the preferred embodiments described herein, but rather is defined by the claims and equivalents thereof.

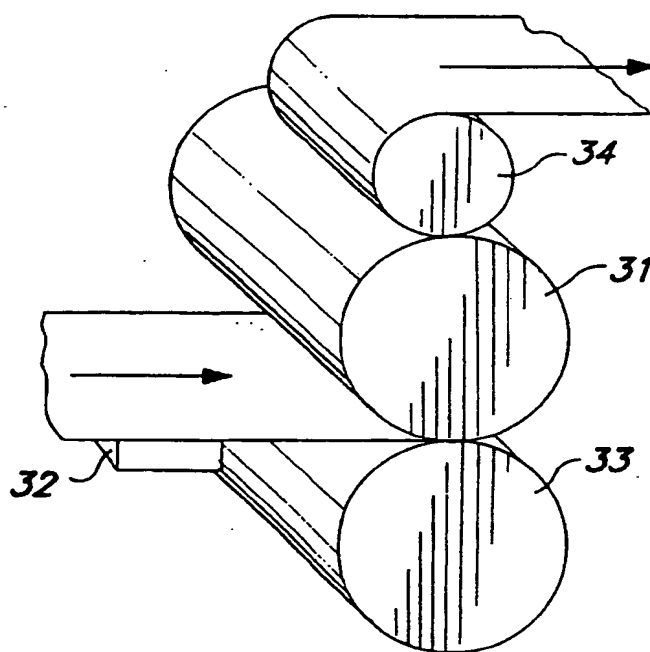
The invention has been thus described, what is claimed as new and desired to  
10 secure by Letters Patent is:

- adapted to absorb oil,
- B. providing a coating of a pre-membrane composition on the said first surface,
- C. heating the coating to convert the coating to a porous membrane having a first side spaced from the substrate and a second side adjacent the substrate, the membrane having an internal surface adapted to convey oil from the first surface of the membrane to the second surface of the membrane.
8. A method as recited in Claim 7, wherein the pre-membrane composition includes polymer particles in a liquid carrier.
9. A method as recited in Claim 7, wherein the pre-membrane composition includes uniform, spherical particles.
10. A method as defined in claim 9 wherein the spherical particles are of approximately 0.5 micron diameter.
11. A method as recited in Claim 7, wherein the pre-membrane composition includes an amount of plasticizer adapted to result in effective adhesion of the porous membrane to the substrate without resulting in blocking the sheeting.
12. A method as recited in Claim 7, wherein following step C., the first side of the coating is embossed to form a diffraction grating or hologram.
13. A method as recited in Claim 7, wherein following step C., the first side of the coating is embossed while thermally softened, and the porosity of the membrane is maintained.

2 / 4



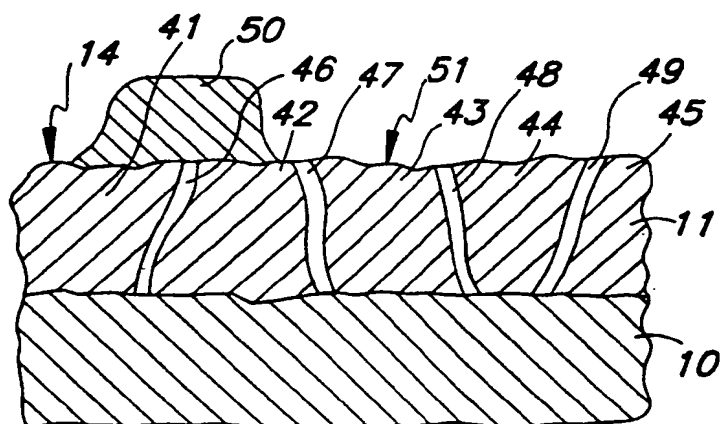
**FIG. 3**



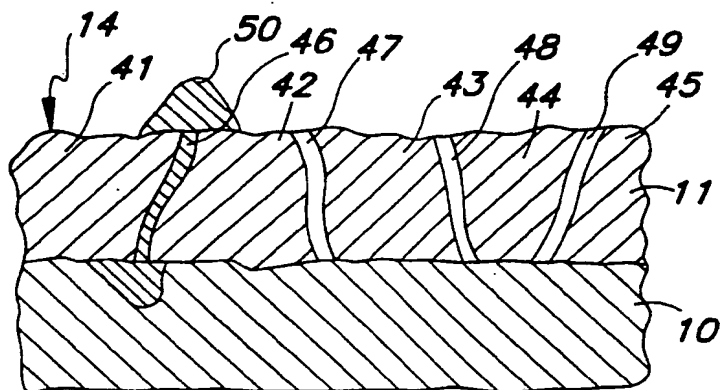
**FIG. 4**

4 / 4

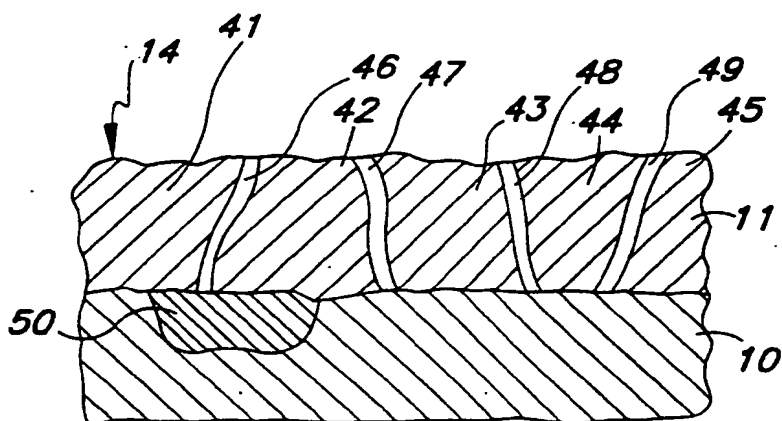
**FIG. 8**



**FIG. 9**



**FIG. 10**



**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. US 9108168  
SA 54510**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
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|   |                     | AU-A- 2610988              | 23-05-89            |
|   |                     | EP-A- 0339079              | 02-11-89            |
|   |                     | US-A- 4913858              | 03-04-90            |
|   |                     | JP-T- 2503408              | 18-10-90            |
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| -----                                     |                     |                            |                     |